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ScienceDirect

Procedia Engineering 87 (2014) 1095 – 1098

Procedia Engineering

www.elsevier.com/locate/procedia

EUROSENSORS 2014, the XXVIII edition of the conference series

An artificial olfactory system (AOS) for detection of highly toxic gases in air based on $YCoO_3$

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Abstract

An artificial olfactory system (AOS) for the detection of highly toxic gases in air is presented. The AOS is based on $YCoO_3$ perovskites. Previous researches of the authors already showed that $YCoO_3$ is characterized by a satisfactory sensitivity toward CO, by a large response speed, and by a very low cross sensitivity to water vapor and hydrocarbons. The sensors used in the AOS are based on non-stoichiometric materials or on materials containing platinum or palladium. The introduction of defects allowed to modify the gas sensing properties and to tune the sensor array to the selected application. Satisfactory results, in terms of sensitivity, selectivity, response speed, power consumption and stability, were obtained with mixtures of air and CO and NO_x.

Peer-review under responsibility of the scientific committee of Eurosensors 2014

Keywords: Metal oxide sensors, artificial olfactory systems, chemiresitors, resistive gas sensors, perovskite materials.

1. Introduction

Standard air pollution measurements are often based on time-consuming and expensive analytical techniques. Artificial olfactory systems (AOS) based on resistive gas sensors, and in particular metal oxides (MOX) chemiresistors, have been considered promising alternatives to these expensive techniques due to their low cost, high sensitivity, fast response. However, the performance of MOX sensors including accuracy, selectivity, reliability,

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Peer-review under responsibility of the scientific committee of Eurosensors 2014
doi:10.1016/j.proeng.2014.11.355

and low sensitivity to interfering gases must be further improved to meet the requirements of standard air pollution measurements. Some air pollutants, called criteria air pollutants, are particularly relevant because they can injure health, harm the environment and cause property damage. Among current criteria pollutants there are Carbon Monoxide (CO), Nitrogen Dioxide (NO_2) and Nitrogen Monoxide (NO), besides Ozone (O_3) and Sulfur Dioxide (SO_2). In this paper we present an AOS aimed at monitoring in particular NO_x and CO. To this purpose the suitability of gas sensors realized with doped and defective $YCoO_3$ perovskites [1] is studied, and an AOS exploiting an array of sensors realized with these materials is proposed.

Non-stoichiometric materials or samples containing platinum or palladium were prepared and characterized with mixtures of dry or humid air, CO and/or NO_x. The idea of modifying the basic structure of the materials with the introduction of different surface and/or bulk defects comes in the attempt of tuning the array to the selected application [1-3].

2. Material preparation and characterization

In this work nano-structured $YCoO_3$ powders were prepared by sol-gel. A water solution of $Y(NO_3)_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and citric acid is heated until it becomes a sol and then a gel, which is finally heated at 900°C.

Different semiconductors were obtained by preparing defective perovskites of the types $YCo_{1-x}O_3$ or $Y_{1-x}CoO_3$, selecting the salts concentrations in order to obtain an Y:Co molar ratio of 1:(1-x) or the inverse, respectively, with x in the range 0.01-0.1. Moreover $YCo_{1-x}Pd_xO_3$ and $YCo_{1-x}Pt_xO_3$ powders were prepared by partly substituting Co with Pd (or Pt), introduced, as usual, via Pd nitrate or acetate (or Pt acetylacetonate) to the mixture of nitrates of Y and Co with Co:Pd (or Ptacac) moles ratio in the range 0.03 – 0.1 before heating. Finally surface impregnation with metallic Pd and Pt was obtained putting the prepared powders in a solution with $Pd(NO_3)_2$ or $Pd(CH_3COO)_2$ in various percentages. The prepared powders were characterized in terms of composition and microstructure using XRD and SEM-EDX methods; moreover, the surface properties of these powders were investigated by means of TPD and TPR, respectively. The compounds crystallize in the perovskite form in nanoporous powders with average crystallite size of 400 nm (figure 1a).

3. Gas sensing properties assessment

Some sensors hosting sensing films obtained from the prepared powders were realized by screen-printing technique (see figure 1b) [4]. The electric properties and responses to CO and NO_x were evaluated.

To test the sensors, a system was used [4] that individually controls the film temperatures or measures them with a resolution of about 0.1 °C, and that allows to accurately set the measurement conditions: gas concentrations and flow, chamber temperature and humidity.

The sensor response, *r*, is obtained with measurements under a constant gas flow (200 mL/min) and is defined as follows:

$$r = (R-R_0)/R_0 \quad (1)$$

where R_0 is the baseline resistance value obtained at the considered temperature in a carrier gas, whereas R is the value of the sensor resistance after a fixed-duration exposure to the test gas mixture.

All the $YCoO_3$ based sensors show p-type semiconducting properties in every test environment within the temperature range of 100–380 °C. An example of the obtained response to NO_2 can be seen in figure 2 (left plot). It can be seen that the response is given by the contribution of two different reactions: one implying the oxidation of the surface, which is faster and favored at low temperature, the other reducing the surface, which is slower and favored at higher temperatures. A similar behavior is seen for NO. From the literature the following possible routes can be assumed for gas reduction:

$$(NO)_{gas} + S_{NO} \leftrightarrow (NO^- - S_{NO}) + h^+ \qquad (NO_2)_{gas} + S_{NO} \leftrightarrow (NO_2^- - S_{NO}) + h^+ \qquad \text{low T}$$

As can it be seen the target gases oxidize the surface and reduces the resistance because adsorbed NO_x^- enhances the surface density of carriers. The largest response is seen around 180°C.

A possible route for the oxidation of the gas is:

$$(NO)_{gas} + (O^- - S_O) + h^+ \leftrightarrow (NO_2)_{gas} \quad (NO_2)_{gas} + (O^- - S_O) + h^+ \leftrightarrow (NO)_{gas} + (O_2)_{gas} \qquad \text{high T}$$

Related to these reactions an increase in the resistance is expected. This is a weaker effect, in fact a low amount of adsorbed oxygen on the grain surface is expected; only Pd doped sensors show an appreciable response related to this behavior over 200°C.

a) b)

Fig. 1 a) SEM image of the prepared powder b) Sensors and front end electronics of the characterization system

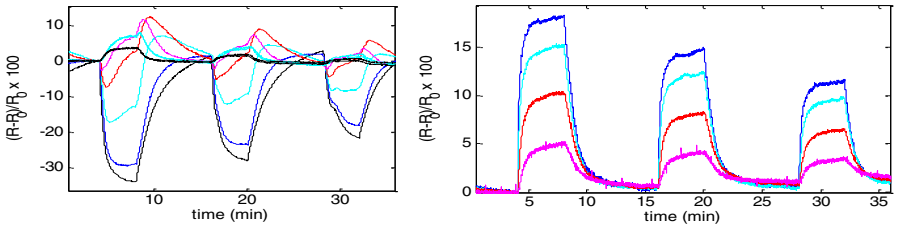

Fig. 2 – left: typical response to NO_2 at different temperatures; right: typical response to CO.

The response to CO was studied using both air and an inert carrier; the results seem to indicate that the main chemical reaction involved in the response is the direct adsorption on the surface so the response in air results lower that the one in N_2. The only material which shows a better sensitivity in air, especially at high temperature, is $YCoO_3$ heavily modified by insertion of Pd in the lattice. The prepared sensors have a low response to CO for temperatures below 200°C. The responses of the different materials are shown in figure 3. Moreover, the typical response values, response time (10%-90% T_{res}) and recovery time (90%-10% T_{rec}) are compared (at the optimum temperatures and at fixed test gas concentration) in Tab. I for some selected materials.

4. AOS development and tests

Sensors doped with Pd were selected for CO detection. In fact, if used at temperatures around 280 °C, they show a satisfactory sensitivity and a large response speed. For NO_2 sensing defective materials (in Co) were selected which give a good sensitivity, a fast response (response time, $T_{10\%-90\%}$=1 min, and recovery time, $T_{90\%-10\%}$=3 min) at a temperature close to 180°C. For NO sensing the stoichiometric material was selected. Finally, the selected sensors were tested with mixtures of NO_x and CO in dry and humid air, confirming that also in presence of the two target gases the responses of the individual sensors can be used to identify a single component. The behavior of two different powders are shown in fig. 4. Some tests in humid environment have been performed, with RH=40% (40 °C) and the response of the tested materials remains almost the same as in dry environment above 180°C.

Conclusions

An AOS was developed which allows to detect CO and NO_x in humid air. The proposed system provides a satisfactory selectivity with respect to CO and NO_x, a fast response and a satisfactory long term stability.

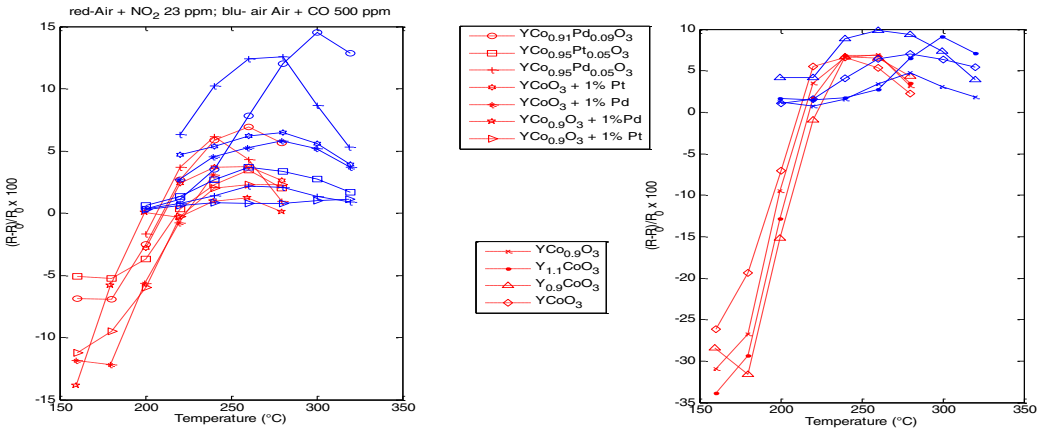

Fig.3 – Responses of different materials to: Air +23 ppm NO_2 (red), Air +500 ppm CO (blu).

Table 1. Selected material characteristics

	Air+CO		Air+NO_2		Air+NO	
$YCo_{0.91}Pd_{0.09}O_3$	300°C	T_{resp}=0.6 min T_{rec}=2.5 min r=15% @500ppm	180 °C	T_{resp}=0.6 min T_{rec}=2 min r=-7% @20ppm	180°C	T_{resp}=1 min T_{rec}=3.8 min r=-5% @10ppm
$YCo_{0.9}O_3$	270°C	T_{resp}=1.3 min T_{rec}=3.2 min r =5% @500ppm	180°C	T_{resp}=0.8 min T_{rec}=2 min r=-30% @23ppm	180°C	T_{resp}=0.8 min T_{rec}=1.5 min r=-20% @23ppm
$YCoO_3$	260°C	T_{resp}=1.5 min T_{rec}=4.7 min r=5% @500ppm	180 °C	T_{resp}=0.5 min T_{rec}=1 min r=-18% 23ppm	210°C	T_{resp}=0.5 min T_{rec}=0.6 min r=-15% @23ppm

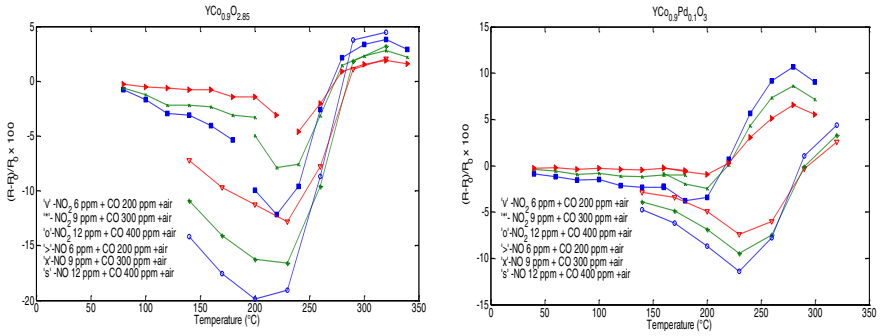

Fig. 4- Response of the different materials to mixtures of CO and NO or NO_2 (air carrier gas) as a function of temperature. The sensitivity to NO_x at low temperatures is not affected by the presence of CO, that interacts with the surface at the highest end of the tested temperature range.

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